

2

OFFICE OF NAVAL RESEARCH

AD-A259 148



GRANT N00014-89-J-3198

R&T Code b41c013dar

Technical Report No. 12

"A μ -Pyrazolyl Terpyridineplatinum(II) Dimer"

by

J. A. Bailey and H. B. Gray

Published in Acta. Cryst

California Institute of Technology
Division of Chemistry
Pasadena, CA. 91125

August 1992

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

This document has been approved for public releases and sale: its distribution is unlimited.

Accession For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

DTIC
ELECTE
JAN 08 1993
S E D

93-00469



REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>THIS REPORT IS THE PROPERTY OF THE U.S. GOVERNMENT. IT IS TO BE REPRODUCED BY ANYONE without fee or charge, and its use is unlimited. It is to be distributed to the public by the National Technical Information Service (NTIS) and to the public by the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE	3. REPORT TYPE AND DATES COVERED Technical	
4. TITLE AND SUBTITLE A u-Pyrazolyl Terpyridineplatinum(II) Dimer.			5. FUNDING NUMBERS G N00014-89-J3198	
6. AUTHOR(S) J. A. Bailey and H. B. Gray				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Division of Chemistry California Institute of Technology Pasadena, CA. 91125			8. PERFORMING ORGANIZATION REPORT NUMBER 12	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Chemistry Division 800 N. Quincy Street Arlington, VA. 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT This document has been approved for public release and sale: its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) μ -(Pyrazolyl- <i>N:N'</i>)-bis[(2,2,2"-terpyridine)platinum(II)] perchlorate acetonitrile solvate, [Pt ₂ (C ₁₅ H ₁₁ N ₃) ₂ (C ₃ H ₃ N ₂)](ClO ₄) ₃ .CH ₃ CN, <i>M_r</i> = 1263.18, orthorhombic, <i>Pnma</i> <i>a</i> = 18.172 (2), <i>b</i> = 17.950 (3), <i>c</i> = 12.086 (4) Å, <i>V</i> = 3942.3 (15) Å ³ , <i>Z</i> = 4, <i>D_x</i> = 2.128 g cm ⁻³ , λ(Mo Kα) = 0.71073 Å, μ = 74.41 cm ⁻¹ , <i>F</i> (000) = 2416, room temperature (297K), <i>R</i> = 0.0337 for 2510 reflections with <i>F_o</i> ² > 3σ(<i>F_o</i> ²). A single pyrazolyl unit bridges two Pt centres. The square-planar coordination around each Pt atom is completed by a tridentate terpyridine ligand. The Pt...Pt separation is 3.432 (1) Å with an inclination of 47.7 (12)° between the two Pt square planes.				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

C920074-HH585 AC17\AC2968-1

 μ -PYRAZOLYL TERPYRIDINEPLATINUM(II) DIMER

JAMES A. BAILEY AND HARRY B. GRAY

Acta Cryst. (1992). C48, 0000-0000A μ -Pyrazolyl Terpyridineplatinum(II) Dimer

BY JAMES A. BAILEY* AND HARRY B. GRAY

Division of Chemistry and Chemical Engineering† and The Beckman Institute, Mail Code 139-74,
California Institute of Technology, Pasadena, California 91125, USA

(Received 16 September 1991; accepted 14 January 1992)

* To whom correspondence should be addressed.

† Contribution No. 8503.

Abstract. μ -(Pyrazolyl-*N,N'*)-bis[(2,2',2''-terpyridine)platinum(II)] perchlorate acetonitrile solvate, $[\text{Pt}_2(\text{C}_5\text{H}_4\text{N}_2)_2(\text{C}_3\text{H}_3\text{N}_3)](\text{ClO}_4)_3 \cdot \text{CH}_3\text{CN}$, $M_r = 1263.18$, orthorhombic, $Pnma$, $a = 18.172$ (2), $b = 17.950$ (3), $c = 12.086$ (4) Å, $V = 3942.3$ (15) Å³, $Z = 4$, $D_x = 2.128$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 74.41$ cm⁻¹, $F(000) = 2416$, room temperature (297 K), $R = 0.0337$ for 2510 reflections with $F_o^2 > 3\sigma(F_o^2)$. A single pyrazolyl unit bridges two Pt centres. The square-planar coordination around each Pt atom is completed by a tridentate terpyridine ligand. The Pt...Pt separation is 3.432 (1) Å with an inclination of 47.7 (12)° between the two Pt square planes.

Introduction. We are currently investigating the properties of binuclear terpyridineplatinum(II) complexes. The compound (μ -pz)bis(terpy)Pt(ClO₄)₃ (pz = pyrazolyl, terpy = terpyridine) is one of a series of binuclear complexes that have been synthesized in which the interplatinum distance is varied. The effect of the Pt-atom separation on absorption and emission spectra can be readily studied with these complexes.

Experimental. This material was synthesized by heating an aqueous solution of [Pt(terpy)Cl]Cl and pyrazole (1/2 equiv.) (pH adjusted to ca 9 with 1M NaOH) to 348 K for 5 d. The orange-red solution slowly changed to pale orange. Cooling and addition of NaClO₄ precipitated the product as a perchlorate salt. Crystals for X-ray analysis were grown by slow evaporation of an acetonitrile solution. A pale orange tabular block crystal, 0.22 × 0.42 × 0.60 mm; was used for data collection on a CAD-4 diffractometer, with ω -scan technique 25 reflections with $34 < 2\theta < 41^\circ$ were used for determination of the cell dimensions. An empirical absorption correction based on ψ scans of six reflections, with relative transmission from 0.508 to 1.388, was applied. $(\sin\theta/\lambda)_{\text{max}} = 0.54$; h from -14 to 14, k from -21 to 21, l from 0 to 17. Three standard reflections (153,

411, 342) showed decay of 0.6% in 148 h of data collection; data were corrected for this decay. 14841 reflections were measured, of which 3588 were independent. Goodness of fit for merging was 1.35 (R_{merge} for 378 reflections with exactly two observations, 0.0175). All reflections were used in solution and refinement of the structure. Coordinates of the Pt atom were found from a Patterson map, remaining heavy atoms were found by successive structure factor - Fourier calculations, including an acetonitrile molecule of crystallization and two perchlorate ions. F_o^2 magnitudes were used in full-matrix least-squares refinement, which minimized $\sum w(F_o^2 - F_c^2)^2$. H atoms were positioned by calculation (C-H = 0.95 Å) and included as constant contributors to the structure factors. H atoms on the acetonitrile were calculated for two possible positions based on the symmetry of the mirror plane which contains the CH₃CN molecule; difference and Fourier maps did not favor either conformation so both positions were included, each contributor being set at half occupancy. H-atom parameters were not refined but recalculated once, near the conclusion of the refinement. Positional and anisotropic temperature parameters for all non-H atoms (except O in disordered ClO₄⁻, isotropic), a scale factor and secondary extinction parameter were refined. At convergence, difference maps suggested that the second ClO₄⁻ ion which occupies a special position on a mirror plane might be modeled more appropriately as the superposition of two ions each with half occupancy and sharing both the Cl2 and O6 positions. Although this model accounts for most of the electron density in the area and the average Cl-O bond length is 1.43 Å, the actual bond lengths and angles deviate substantially from a tetrahedral ClO₄⁻ geometry; however, other disorder models did not improve on this result, so refinement was terminated at this stage.

$R = 0.0514$ for 340 reflections with $F_o^2 > 0$, wR (on F^2) = 0.0050 and goodness of fit = 2.01 for 3588 reflections and 293 parameters. Weights were taken as $1/\sigma^2(F_o^2)$; variances [$\sigma^2(F_o^2)$] were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of error plus another additional term, $(0.014I)^2$. In the final least-squares cycles $(\Delta/\sigma)_{\max} = 0.04$; $-0.91 \leq \Delta\rho \leq 1.57 \text{ e \AA}^{-3}$ in the final difference Fourier map, with all large peaks within 1.5 \AA of the Pt atom. Atomic scattering factors and values for $\Delta f'$ were taken from Cromer & Waber (1974) and Cromer (1974). Programs used were those of the CRYM crystallographic computing system (Duchamp, 1964) and ORTEP11 (Johnson, 1976). Final atomic coordinates and U_{eq} are listed in Table 1 with selected distances and angles given in Table 2.*

* Lists of assigned H-atom parameters, complete distances and angles, anisotropic temperature parameters and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55055 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: H110585]

Tables 1,2—

Discussion. Fig. 1 shows the cation viewed along the intermetal axis with atom labels; Fig. 2 is a stereoscopic view of the entire 3+ cation. The geometry around the Pt atoms is nearly square planar, distorted only by the restricted bite angle of the planar terpyridine unit. This results in a short Pt—N3 distance [1.938 (5) Å] and a N2—Pt—N4 *trans* bond angle of only 162.2 (2)°. The remaining bond lengths around the Pt atom are all over 2 Å [2.018 (6), 2.020 (5) and 2.031 (6) Å]. This geometry is entirely consistent with other related Pt(tpy) complexes (Dewan, Lippard & Bauer, 1980; Ratilla, Scott, Moxness & Kostic, 1990; Wong & Lippard, 1977; Jennette, Gill, Sadownick & Lippard, 1976).

Figs. 1,2—

The two Pt atoms are bridged by a single pyrazolyl group, resulting in a Pt...Pt separation of 3.432 (1) Å (parallel, by symmetry, with the y axis) and an inclination between the two square planes of 47.7 (12)°. This distance is intermediate in the range of Pt^{II}...Pt^{II} separations exhibited by other binuclear tpy complexes, that have been observed as short as 2.9884 Å (Ratilla *et al.*, 1990) and as long as 4.420 Å (Dewan *et al.* 1980). The Pt atom is displaced out of the terpyridine plane by *ca* 0.2 Å towards the other Pt atom in the same binuclear unit. The bond lengths and angles within each pyridine ring are characteristic of a delocalized aromatic system, ranging from 1.334 (10) to 1.395 (14) Å and from 117.2 (8) to 124.9 (7)°. Similarly, the bond lengths and angles within the pyrazolyl ring range from 1.331 (13) to 1.340 (9) Å and from 105.1 (9) to 110.5 (8)°, thereby demonstrating the delocalized nature of the π electrons in the five-membered ring.

We thank Larry Henling for his assistance. This work was supported by an NSERC (Canada) Postdoctoral Fellowship to JAB and a grant from the Office of Naval Research (N00014-89-J-3198).

References

- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DEWAN, J. C., LIPPARD, S. J. & BAUER, W. R. (1980). *J. Am. Chem. Soc.* **102**, 858–860.
- DUCHAMP, D. J. (1964). CRYM Crystallographic computing system. *Am. Crystallogr. Assoc. Meet.*, Bozeman, Montana. Paper B14, p.29.
- JENNETTE, K. W., GILL, J. T., SADOWNICK, J. A. & LIPPARD, S. J. (1976). *J. Am. Chem. Soc.* **98**, 6159–6168.
- JOHNSON, C. K. (1976). ORTEP11. Report ORNL-3794, third revision. Oak Ridge National Laboratory, Tennessee, USA.
- RATILLA, E. M. A., SCOTT, B. K., MOXNESS, M. S. & KOSTIC, N. M. (1990). *Inorg. Chem.* **29**, 918–926.
- WONG, Y.-S. & LIPPARD, S. J. (1977). *J. Chem. Soc. Chem. Commun.* pp. 824–825.

C920074-HH585 AC17\AC2968-2

Table 1. Final refined atomic coordinates ($\times 10^4$) and equivalent isotropic ($\text{\AA}^2 \times 10^4$)/isotropic (\AA^2) temperature factors for μ -pyrazolyl terpyridine platinum dimer

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}/B^{\dagger}
Pt	769 (.1)	1544 (.1)	773 (.2)	436 (1)
N1	1651 (3)	2128 (3)	1306 (4)	519 (14)
N2	221 (3)	1425 (3)	2227 (5)	531 (16)
N3	-97 (3)	1032 (3)	230 (5)	482 (15)
N4	1067 (3)	1445 (3)	-829 (5)	550 (16)
C1	2318 (4)	1911 (4)	1652 (7)	742 (26)
C2	2745 (5)	2500	1840 (10)	676 (33)
C3	443 (4)	1620 (5)	3238 (6)	619 (20)
C4	10 (5)	1515 (5)	4129 (7)	777 (25)
C5	-681 (5)	1190 (5)	4040 (7)	756 (26)
C6	-899 (4)	506 (5)	3011 (7)	670 (23)
C7	-447 (4)	1081 (4)	2096 (6)	519 (19)
C8	-630 (3)	874 (4)	965 (6)	501 (21)
C9	-1271 (4)	542 (4)	570 (8)	653 (24)
C10	-1347 (4)	426 (5)	-521 (8)	710 (24)
C11	-797 (5)	604 (5)	-1273 (7)	746 (25)
C12	-153 (4)	920 (4)	-872 (6)	518 (20)
C13	511 (5)	1127 (4)	-1465 (7)	596 (23)
C14	631 (5)	993 (5)	-2565 (8)	804 (27)
C15	1319 (7)	1148 (6)	-3024 (8)	899 (31)
C16	1856 (5)	1429 (5)	-2375 (9)	878 (29)
C17	1725 (4)	1580 (4)	-1281 (7)	667 (21)
C1	1776 (1)	169 (1)	3969 (2)	637 (5)
O1	1012 (3)	12 (3)	3858 (5)	844 (17)
O2	1883 (3)	920 (3)	4340 (5)	933 (19)
O3	2096 (3)	-323 (4)	4753 (5)	1018 (20)
O4	2142 (3)	103 (4)	2928 (5)	985 (19)
C12	3943 (2)	2500	8099 (3)	971 (12)
O5	4294 (11)	2500	6855 (18)	9.7 (6) [†]
O6	4620 (10)	2500	8521 (14)	17.9 (6) [†]
O7	3500 (12)	2097 (12)	7490 (17)	16.4 (7) [†]
O8	3366 (14)	2500	9120 (19)	11.9 (7) [†]
O9	3944 (9)	1774 (11)	8288 (14)	10.8 (5) [†]
N5	3957 (8)	2500	4114 (13)	1237 (50)
C18	2712 (9)	2500	5083 (12)	1037 (49)
C19	3412 (9)	2500	4573 (12)	837 (43)

[†] Isotropic displacement parameter.Table 2. Selected distances (\AA) and angles ($^{\circ}$) for μ -pyrazolyl terpyridineplatinum dimer

Pt—N1	2.020 (5)	Pt—N2	2.031 (6)
Pt—N3	1.938 (5)	Pt—N4	2.018 (6)
N1—C1	1.340 (9)	N1—N1	1.335 (7)
N2—C3	1.334 (10)	N2—C7	1.370 (9)
N3—C8	1.345 (9)	N3—C12	1.350 (9)
N4—C13	1.391 (10)	N4—C17	1.337 (10)
C1—C2	1.331 (13)	C3—C4	1.347 (12)
C4—C5	1.388 (13)	C5—C6	1.366 (12)
C6—C7	1.393 (11)	C7—C8	1.456 (10)
C8—C9	1.392 (11)	C9—C10	1.342 (12)
C10—C11	1.389 (12)	C11—C12	1.388 (11)
C12—C13	1.451 (11)	C13—C14	1.370 (12)
C14—C15	1.395 (14)	C15—C16	1.349 (14)
C16—C17	1.371 (13)		
N2—Pt—N1	99.7 (2)	N3—Pt—N1	177.0 (2)
N4—Pt—N1	98.0 (2)	N3—Pt—N2	81.1 (2)
N4—Pt—N2	162.2 (2)	N4—Pt—N3	81.4 (2)
C1—N1—Pt	131.8 (5)	N1—N1—Pt	121.3 (4)
N1—N1—C1	106.9 (5)	C3—N2—Pt	128.1 (5)
C7—N2—Pt	112.5 (4)	C7—N2—C3	119.4 (6)
C8—N3—Pt	117.5 (4)	C12—N3—Pt	117.7 (4)
C12—N3—C8	124.5 (6)	C13—N4—Pt	111.8 (5)
C17—N4—Pt	128.0 (5)	C17—N4—C13	119.9 (6)
C2—C1—N1	110.5 (8)	C1—C2—C1	105.1 (9)
C4—C3—N2	121.3 (7)	C5—C4—C3	121.7 (8)
C6—C5—C4	117.2 (8)	C7—C6—C5	120.5 (7)
C6—C7—N2	119.9 (6)	C8—C7—N2	115.2 (6)
C8—C7—C6	124.9 (7)	C7—C8—N3	113.7 (6)
C9—C8—N3	117.8 (6)	C9—C8—C7	128.5 (7)
C10—C9—C8	119.3 (7)	C11—C10—C9	122.2 (8)
C12—C11—C10	118.2 (8)	C11—C12—N3	117.9 (7)
C13—C12—N3	112.8 (6)	C13—C12—C11	129.3 (7)
C12—C13—N4	115.8 (7)	C14—C13—N4	119.5 (7)
C14—C13—C12	124.6 (7)	C15—C14—C13	119.6 (8)
C16—C15—C14	119.4 (9)	C17—C16—C15	120.6 (9)
C16—C17—N4	120.8 (8)		

Fig. 1. A labelled ORTEP (Johnson, 1976) drawing of the cation with 50% probability ellipsoids viewed down the intermetal axis. H atoms are not shown.

Fig. 2. An ORTEP (Johnson, 1976) stereoscopic drawing showing the complete cation. Atoms are shown as 50% probability ellipsoids.

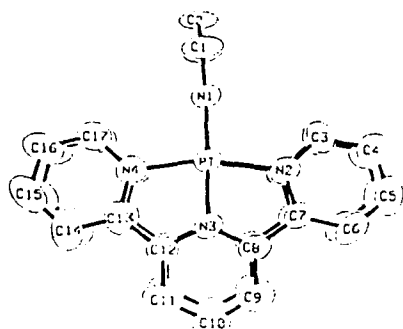


Fig. 1

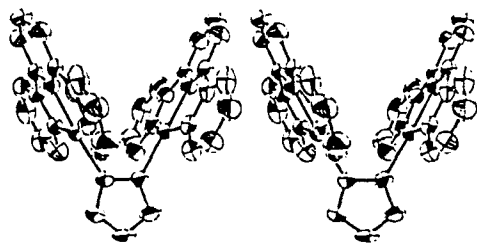


Fig. 2